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WASTE INCINERATION FOR RESOURCE RECOVERY IN REGENERATIVE LIFE SUPPORT SYSTEMS

NASA Cooperative Agreement No. NCC 2-851

Yearly Report

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Introduction

This report covers the period of performance from July 1995 through the end of August 1996. During this time, the combustor system was completed and initial testing was begun. Results of the initial tests are presented below. Small scale tests of the copper oxide cleanup system were also started and results are discussed.

As previously reported, the combustion system chosen was a fluidized bed incinerator. This system allows for low, uniform temperatures and limited fuel preparation, and it is commonly used for sludge and biomass systems. The gas cleanup system is a copper oxide adsorbent/catalyst with ammonia as a reagent.

Presently, the project is on schedule as discussed in prior reports (see Technical Requirements and Design Selection Documents).

Summary of Design and Construction of Incineration System

The design feedrate for the system is approximately 12 kg/day, the waste generation rate of inedible biomass, human waste, and some trash components (paper, leftover food) for a 4-person crew. The highest moisture content considered will be 70%.

The fluidized bed is shown in Figure 1. The bed is 6 inches in diameter and approximately 7 feet high. There are 9 1-kWatt heaters surrounding the bed. One, 1-kW heater is used for air preheat. A double screw feeder is envisioned with feed approximately 4 inches above the distributor plate.

Presently 5 kg of bed material (sand and alumina) have been tested in the reactor. The fluidization tests have shown that approximately 200 standard cubic feet per hour (scfh) of air are needed at ambient conditions to fluidize a bed of sand. This corresponds to 70 scfh at 1400 F; if using 20% excess air for combustion, approximately 120 scfh are needed. These calculations indicate that the amount of air required to burn the waste is on the order of that needed to fluidize the bed.

The next section, **Combustion Data**, discusses the detailed results from burning sawdust and hay. Hay was chosen as a surrogate for inedible biomass since the ultimate analysis and the amount of potassium in the ash are similar to inedible biomass, as shown in Table 1.

The potassium is an important parameter since, as discussed previously, the potassium can react with the silica and alumina components in the bed to form low-melting point eutectics. This is illustrated in Figure 2 which shows an SEM of pure sand (b) and sand from the bed after combustion of hay at 1400 F. As seen in this picture, the pure sand has distinct particles.

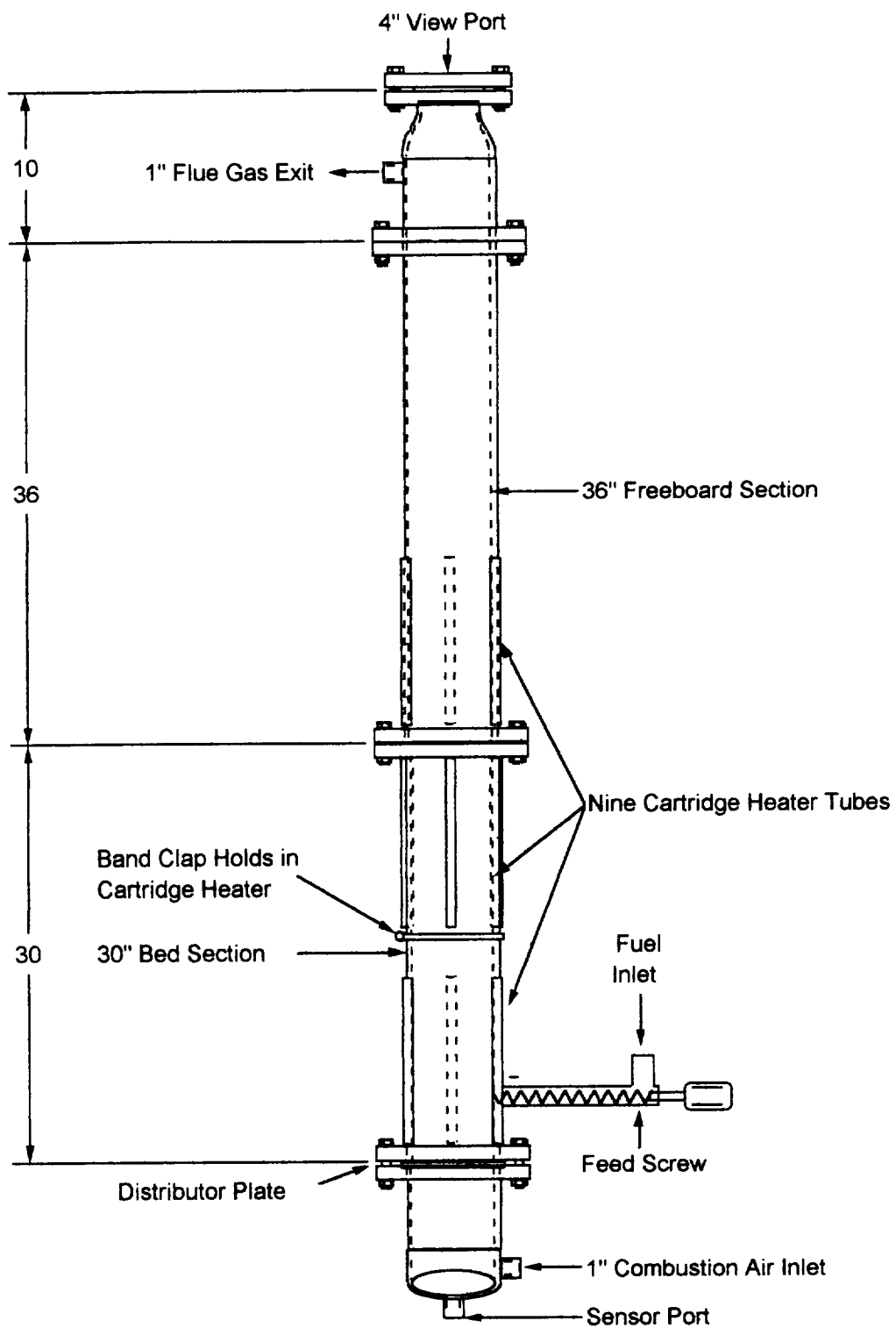


Figure 1. Fluidized Bed Combustor

Analysis of these particles showed that the composition was predominately Si and Al. Figure 2(a) shows the sand particle after combustion. A smooth surface is evident. Analysis of this surface indicated that, in addition to Si and Al, large amounts of K and Ca were evident. Clearly, the smooth surface is a result of melting of the hay since the components of the ash were found.

Table 1. Analysis of Hay and Inedible Biomass

Component	Biomass	Hay
ULTIMATE ANALYSIS		
(% dry)		
Carbon	43.99	44.88
Hydrogen	5.54	5.71
Nitrogen	1.4	1.66
Sulfur	0.15	0.17
Ash	9.75	5.68
Oxygen	39.17	41.90
ASH ANALYSIS		
(%, major components)		
SiO ₂	7.88	4.24
CaO	5.56	17.70
Na ₂ O	0.28	1.63
K ₂ O	58.50	36.10



(a)



(b)

Figure 2. Scanning Electron Micrographs of a Clump of Sand from the FBC (a) and "Pure" Sand (b)

Combustion Data

Species concentrations were determined using several continuous emissions analyzers. Nitrogen oxides were measured with a Thermo Environmental Instruments (Model 42C) chemiluminescent analyzer, oxygen was measured with a Yokogawa (Model ZA8C) zirconium oxide analyzer, carbon monoxide and carbon dioxide were measured with California Analytical Instruments (Model ZRH) and Anarad (Model AR-600) infrared analyzers, and total hydrocarbons were measured with a flame ionization detector in a heated total hydrocarbon analyzer by VIG Industries (Model 20). Data acquisition and analysis was performed using a personal computer which recorded all measured temperatures and pressures, air flow rates, and all measured species concentrations versus time.

Combustor operating conditions that have been investigated include operation of the fluidized bed combustor for bed temperature conditions ranging from 1300°F to 1700°F. Three different fuel streams were investigated: wood chips with 5% moisture, wood chips with 50% moisture, and hay. The wood chips and hay fuel materials approximate the inedible biomass portion of the materials that will be recycled/incinerated using the current technology. Data has been obtained for a range of excess air conditions corresponding to both fuel-lean and fuel-rich conditions. These conditions correspond to stoichiometric ratios ranging from 0.90 to 1.50.

Overall Performance - Raw Data

Data Acquisition

Data logging of the important operational parameters, as described above, was accomplished for all of the experimental conditions that were investigated. Figure 3 presents a rolling 2 minute average of data that was obtained for one set of experiments. The experimental conditions of Figure 3 were for a bed temperature of 1500°F and a fuel feed of 1.0 lb/hr of wood chips with 5% moisture. Excess air levels were incrementally lowered throughout the set of experiments shown in Figure 3 at each of the vertical lines which mark the time at which the excess air level was changed. The first time period corresponds to a 50% excess air condition ($SR = 1.50$) with subsequent time periods corresponding to excess air levels of 40, 30, 20, 15, 10, and 5% respectively (i.e., $SR = 1.4, 1.3, 1.2, 1.15, 1.1, \text{ and } 1.05$).

Combustion Efficiencies and Mass Balances

The data of Figure 3 indicates complete combustion of the fuel and a good mass balance over the entire system. For instance, the average measured CO_2 and O_2 values corresponding to the 50% excess air condition are 12.96% and 6.91% respectively,

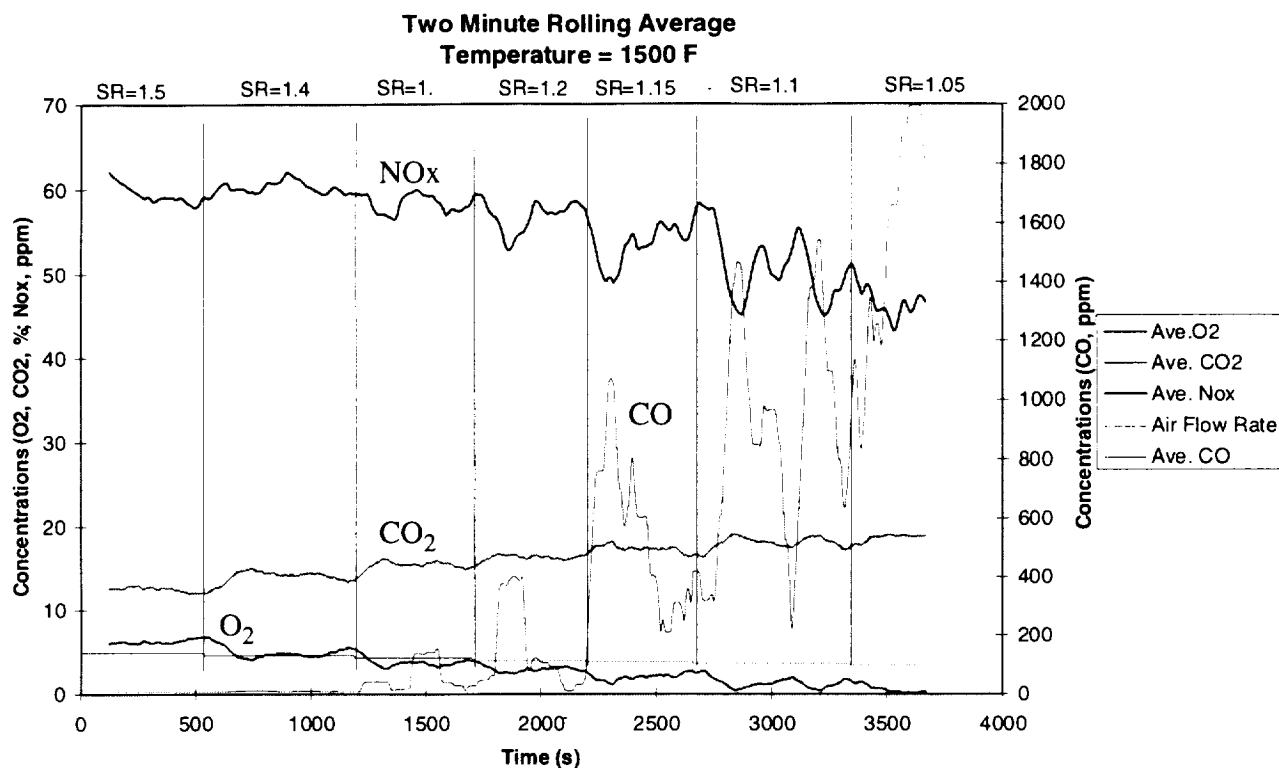


Figure 3. Two-minute rolling average data obtained for feeding of wood chips with 5% moisture, into the fluidized bed at 1500°F, with various levels of excess air.

compared to calculated values for complete combustion of 13.3% CO₂ and 6.9% O₂. Mass balances were similar for all of the data presented herein with measured values of CO₂ and O₂ for fuel-lean conditions that were consistently within 20% of the calculated values.

Solid Fuel Feeder Issues

The fluctuations that are present in each of the data sets in Figure 3 are due to fluctuations in the actual feed rate of the fuel. These fluctuations are present in all of the data sets and are indicative of the difficulties that can be present in achieving steady feeding of solid fuels of non-uniform size and consistency. The double screw feeding method that is currently used can accurately feed these fuels at the desired overall rate (1.0 lb/hr in this case); however, pulsing of the fuel feed rate was consistently observed due to the non-uniformity of the fuel which leads to clumping.

Consistently and steadily feeding inedible biomass and human waste streams requires the design and construction of a new feeder which is currently being pursued with the assistance of a major, high quality bulk solids handling and feeder manufacturer, Accrison, of New Jersey. Samples of inedible biomass have been shipped to Accrison and the company is currently testing a number of possible designs for the final feeding system.

General Trends

The general trends observed in the data of Figure 3 are as follows. As the excess air levels decreases from 50% to 5%, CO concentrations increase from 0 to about 1500 ppm, CO₂ concentrations increase from about 13% to about 18%, O₂ concentrations decrease from about 7% to about 1%, and NO_x levels decrease slightly from about 60 ppm to about 45 ppm. The increases in CO emissions are due to the lowered availability of oxygen as the excess air levels are decreased. The increases in CO₂ are due to decreased dilution of the products with excess air and the reductions in O₂ are due to the decreased air flow rates. The NO_x levels decrease with decreasing excess air levels as would be expected due to decreasing oxygen availability in the NO_x formation regions of the combustor.

Figure 4 presents data similar to that of Figure 3 except the combustor operating conditions are for a bed temperature of 1700°F with a fuel feed of 1.0 lb/hr of wood chips with 50% moisture. The trends observed for these conditions are similar to those of the

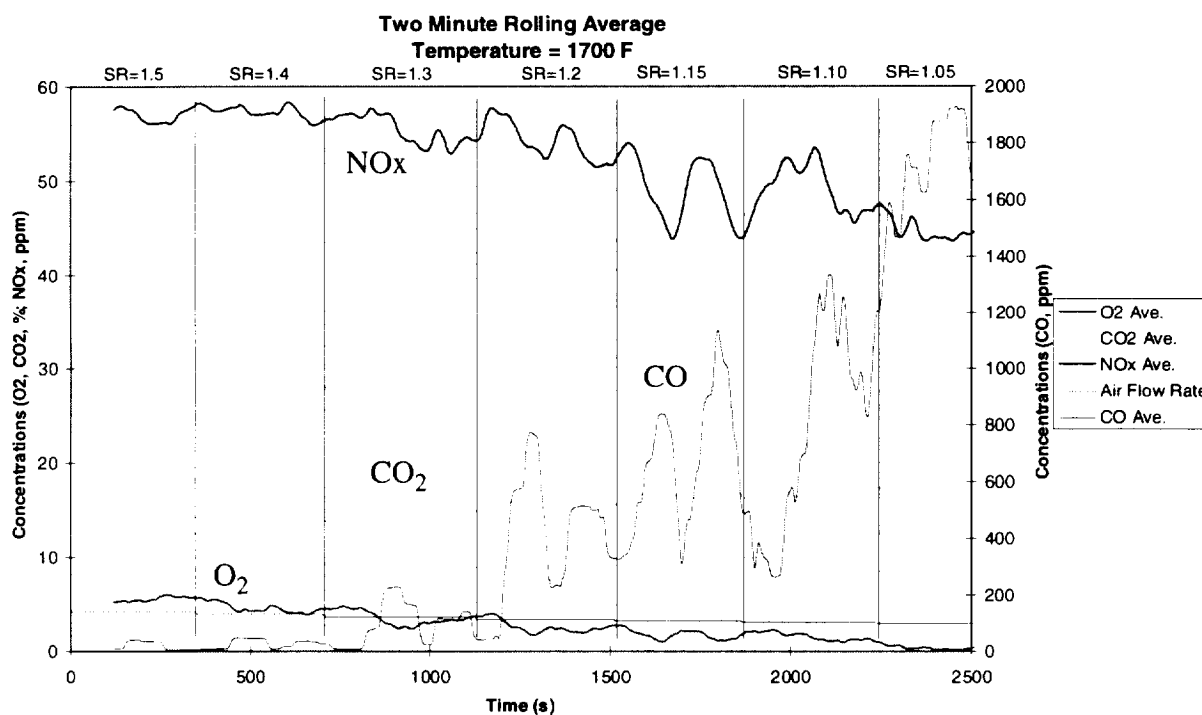


Figure 4. Two-minute rolling average data obtained for feeding of wood chips with 50% moisture, into the fluidized bed at 1700°F, with various levels of excess air.

1500°F bed with 5% moisture in the feed. Notice the increase in CO emissions as the excess air level is lowered, an increase in the CO₂ and a decrease in the O₂ and NO_x as the stoichiometric ratio is changed from 1.50 to 1.05. Also, fluctuations in the measured species concentrations were observed for these conditions as well, and are again attributed to fluctuations in the fuel feed to the system.

Averaging Data and Correcting to 3% O₂

Figure 3 and Figure 4 are presented in this section as examples of the detailed data that was obtained versus time for operation of the fluidized bed combustor. In subsequent sections, average data for each of the conditions will be presented. These average data each represent at least 100 individual measurements obtained under steady-state conditions for each parameter investigated. Also, so that emissions are reported on a consistent basis, they are corrected to 3% O₂ in the exhaust (i.e., the dilution effect that excess air has on measured species concentrations is subtracted out of the data).

Figure 5 presents averaged and corrected results for conditions of 1500°F bed temperature and combustion of wood chips with 5% moisture (i.e., the same conditions as those in Figure 3). Figure 6 presents averaged and corrected data of conditions of 1700°F

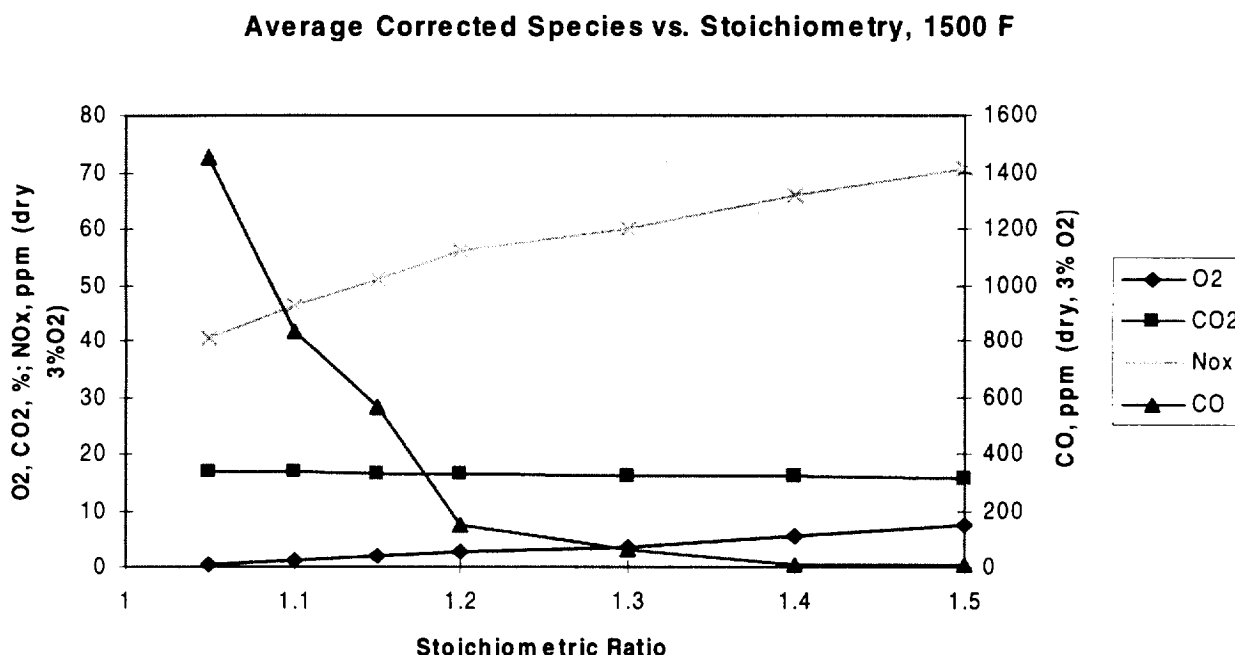


Figure 5. Averaged and corrected data versus stoichiometric ratio for conditions of 1500°F bed temperature and combustion of wood chips with 5% moisture.

bed temperature and the combustion of wood chips with 50% moisture (i.e., the same conditions as those in Figure 4). In each of these figures, averaged data is plotted versus stoichiometric ratio with O₂ and CO₂ given in percent and CO and NO_x given in ppm units. The data presented in Figure 5 and Figure 6 confirm the complete combustion observed in the previous data with the measured and corrected carbon dioxide concentrations are constant with changes in excess air and oxygen concentrations that decrease with decreasing excess air. As stated above, these measured O₂ and CO₂ values fall within 20% of the

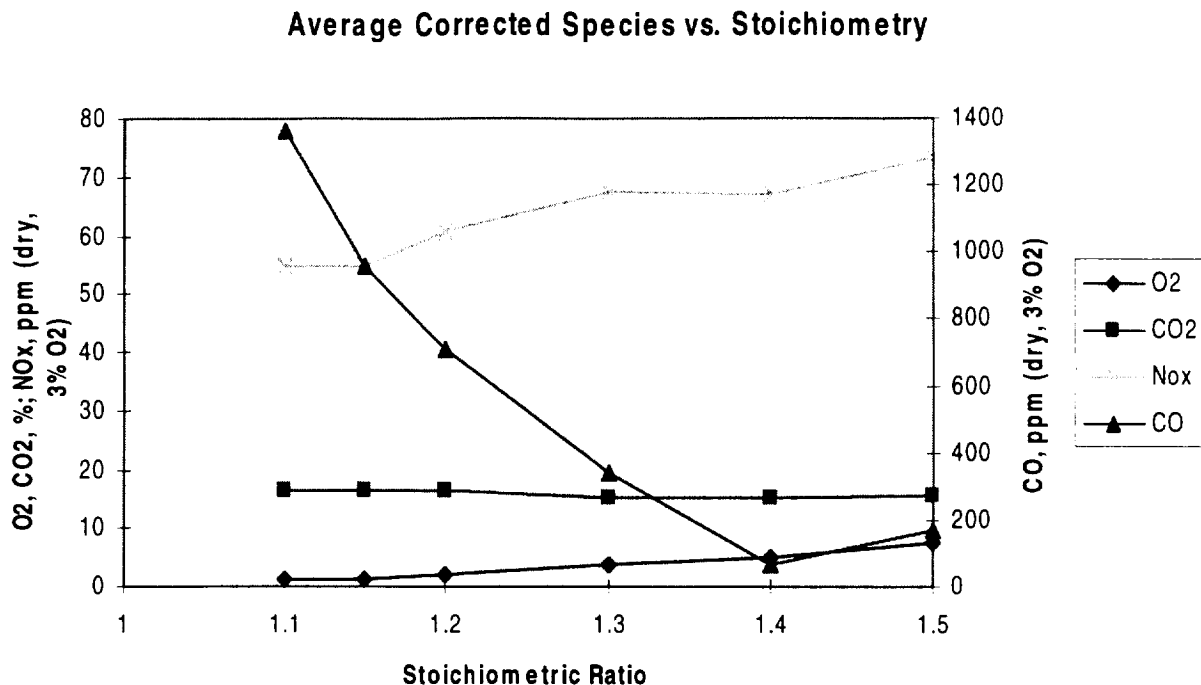


Figure 6. Averaged and corrected data versus stoichiometric ratio for conditions of 1700°F bed calculated values for complete combustion for all of the tests performed on this reactor system.

The oxygen and carbon dioxide values presented above indicate good mass balances and combustion in the fluidized bed combustor that were consistently observed in these investigations. The NO_x and CO emissions data; however, are more dependent upon operating conditions than the other species and are typically of more interest since they are undesirable emissions. The typical CO trend that is observed in this system is one in which the CO increases as excess air is decreased (see Figure 5 and Figure 6). The measured NO_x concentration typically decreased with decreasing excess air (see Figure 5 and Figure 6).

Effects of Temperature

Temperature was measured and recorded at six locations throughout the fluidized bed combustor. The six locations are labeled preheat zone, lower bed, upper bed, lower freeboard, upper freeboard, and exhaust. Temperature was measured at each of these locations using a type-K thermocouple inserted 3 inches into the flow field (i.e., spanning the radius of the reactor). Typical temperature profiles obtained in the reactor are presented in Figure 7. The bed temperature that is used as a reference in this report is the lower bed temperature. Notice that in each case the temperature increases in the upper bed and lower freeboard where it is presumed

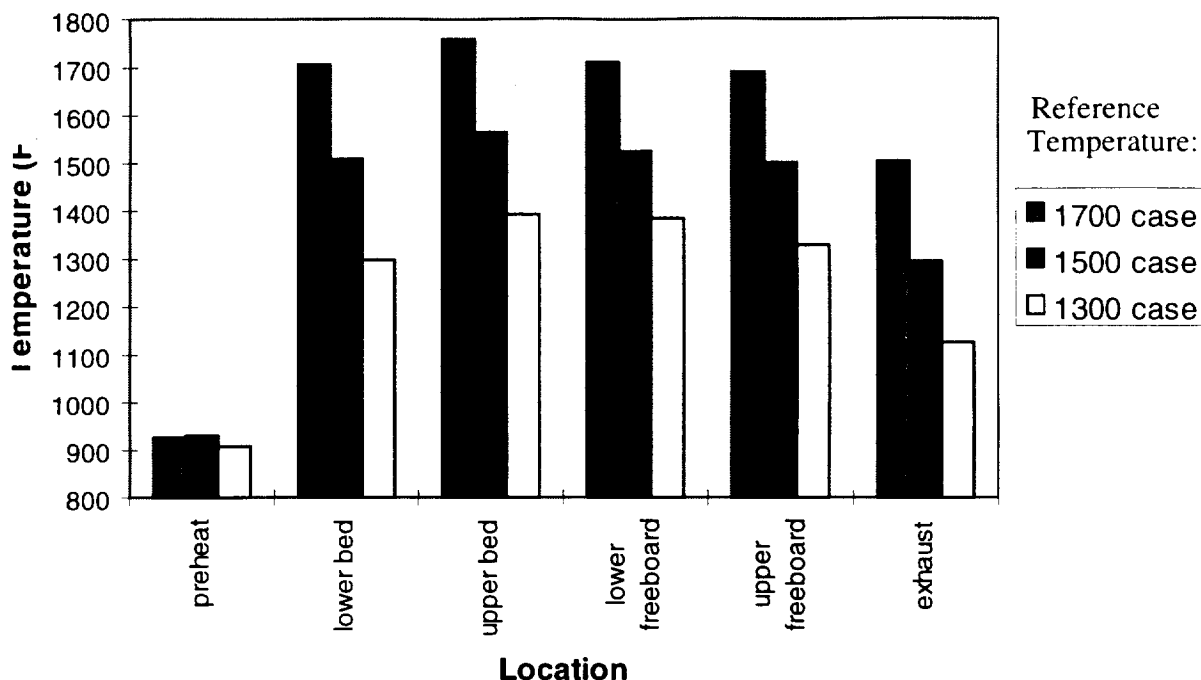


Figure 7. Typical temperature profile in the fluidized bed reactor for 1300°F, 1500°F, and 1700°F bed temperature conditions.

that the gas phase fuel fragments and CO evolve from the bed and are burned. The temperature rise in the upper bed and lower freeboard region for the 1300°F case (about 120°F) was typically slightly greater than that of the 1500 and 1700°F cases (about 90-100°F).

The effects of operating the bed at these three different temperatures on CO that is produced in the system by burning wood that contains 5% moisture is shown in Figure 8. The trend for each of the data sets is one of increasing CO with decreasing stoichiometric ratio (or decreasing excess air). These data indicate that at higher temperature conditions the CO emissions are greater. This was not expected since CO burnout chemical kinetics would suggest that higher CO concentrations would be observed at lower temperature conditions. CO burnout chemical kinetics are exponentially dependent upon temperature. However, it was observed that for the lower bed temperature conditions a flame was stabilized above the bed in the lower freeboard, as opposed to the higher temperature conditions in which all of the combustion appeared to occur in the bed. This suggests that the CO and fuel fragments emitted from the bed under lower bed temperature conditions were sufficiently high in concentration to stabilize a flame above the bed where these species were burned out. Under higher bed temperature conditions, fuel fragments and CO emitted from the bed were lower in concentration (which is consistent with the chemical kinetics) establishing conditions which were not conducive to stabilizing a flame above the bed leading to higher CO emissions.

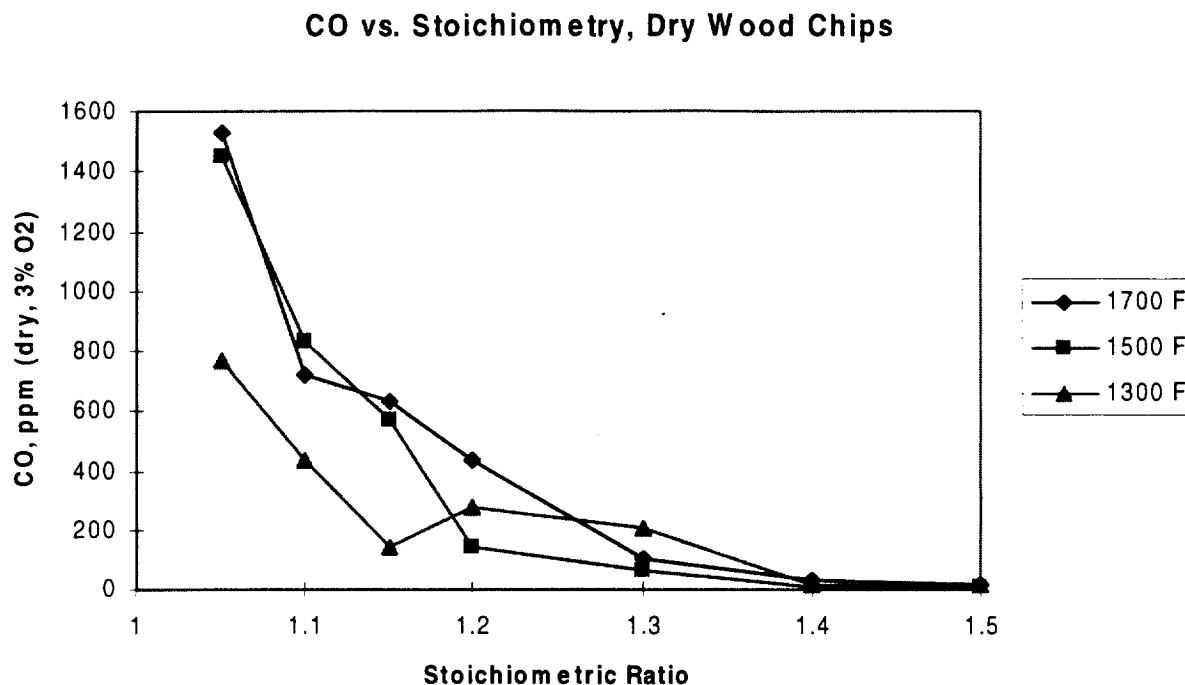


Figure 8. Effect of operating temperature on CO emissions when burning wood chips containing 5% moisture.

Figure 9 presents the NO_x emissions for combustion of wood chips with 5% moisture. For each temperature condition, the NO_x emissions decrease with decreasing stoichiometric ratio. The NO_x emissions are greater for the lower bed temperature conditions, which is again counter-intuitive, unless one considers the presence of a flame in the lower bed temperature cases where the NO_x could be formed. Since temperatures in the fluidized bed are substantially lower than that which is required for substantial thermal NO_x production, most of the NO_x emissions are attributed to fuel nitrogen conversion to NO_x. The wood chips contain approximately 0.1% nitrogen by mass, which translates to approximately 270 ppm at 100% conversion to NO_x.

The effect of operating temperature on the CO emissions obtained from combustion of wood chips containing 50% moisture is presented in Figure 10. As previously observed for the 5% moisture wood chips, CO emissions increase with decreasing stoichiometric ratio. However, the dependence on operating temperature is different than that of the 5% moisture wood chips. At high stoichiometric ratios CO emissions are greater for lower temperature conditions and at low stoichiometric ratios CO is greater for high temperature conditions. This complicated dependence of CO emissions on bed temperature is again attributed to the establishment of a stabilized flame above the bed in which the CO can be burned out.

The CO emissions data presented here suggest that an optimization of the system could be accomplished to provide the desired level of CO. If higher CO was desired at high excess air levels and low bed temperatures, one could increase the moisture content of the fuel. Or if lower

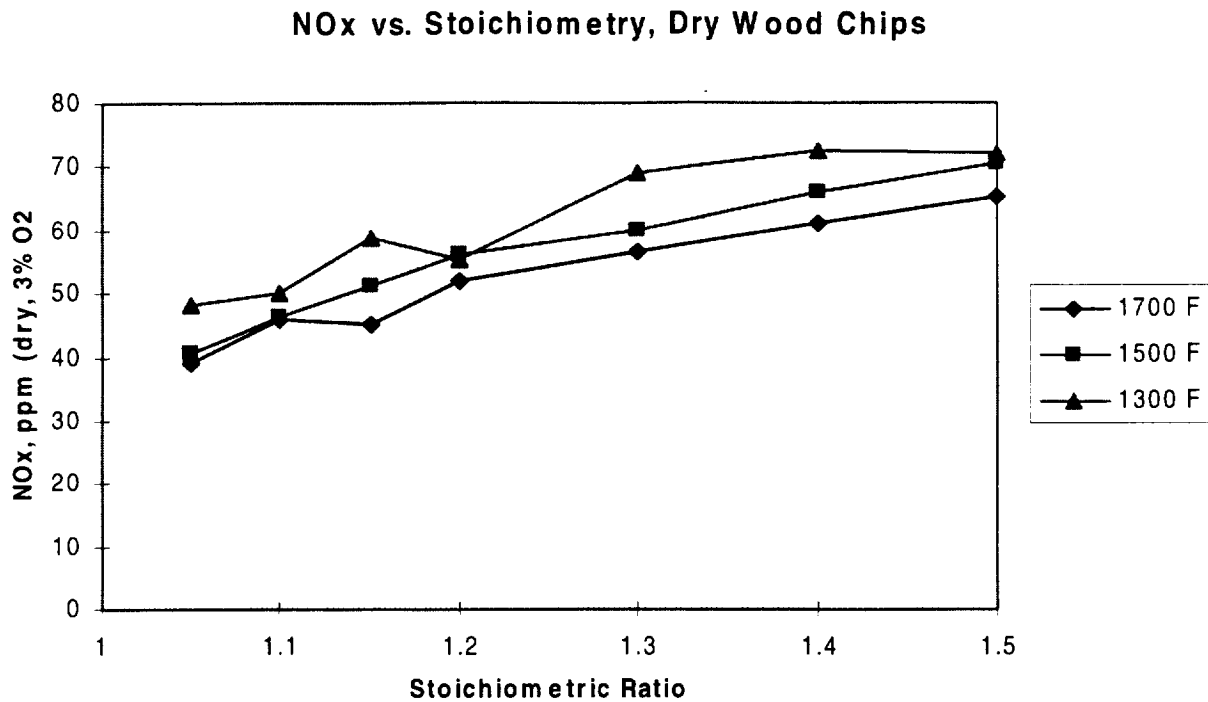


Figure 9. Effect of operating temperature on NOx emissions when burning wood chips containing 5% moisture.

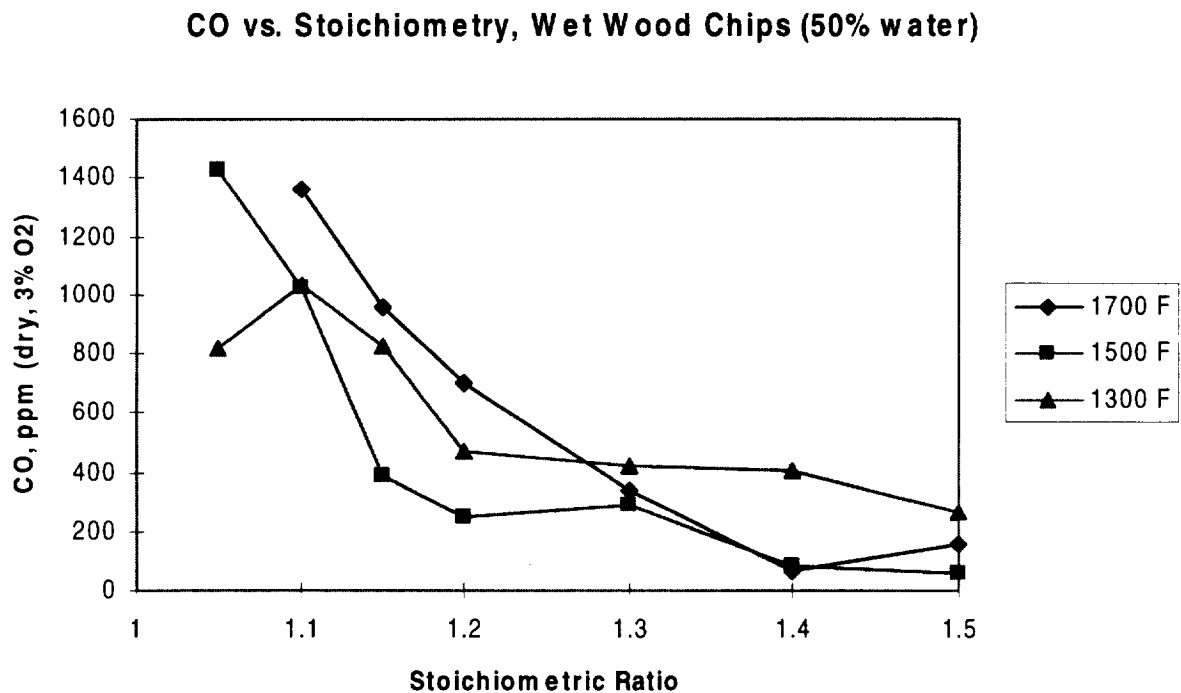


Figure 10. Effect of operating temperature on CO emissions when burning wood chips containing 50% moisture.

excess air levels were desired one could decrease the bed temperature to lower CO emissions or increase the bed temperature to increase CO emissions.

Figure 11 presents NO_x emissions data for combustion of wood chips with 50% moisture. NO_x emissions decrease with decreasing stoichiometric ratio as in the other experiments. The

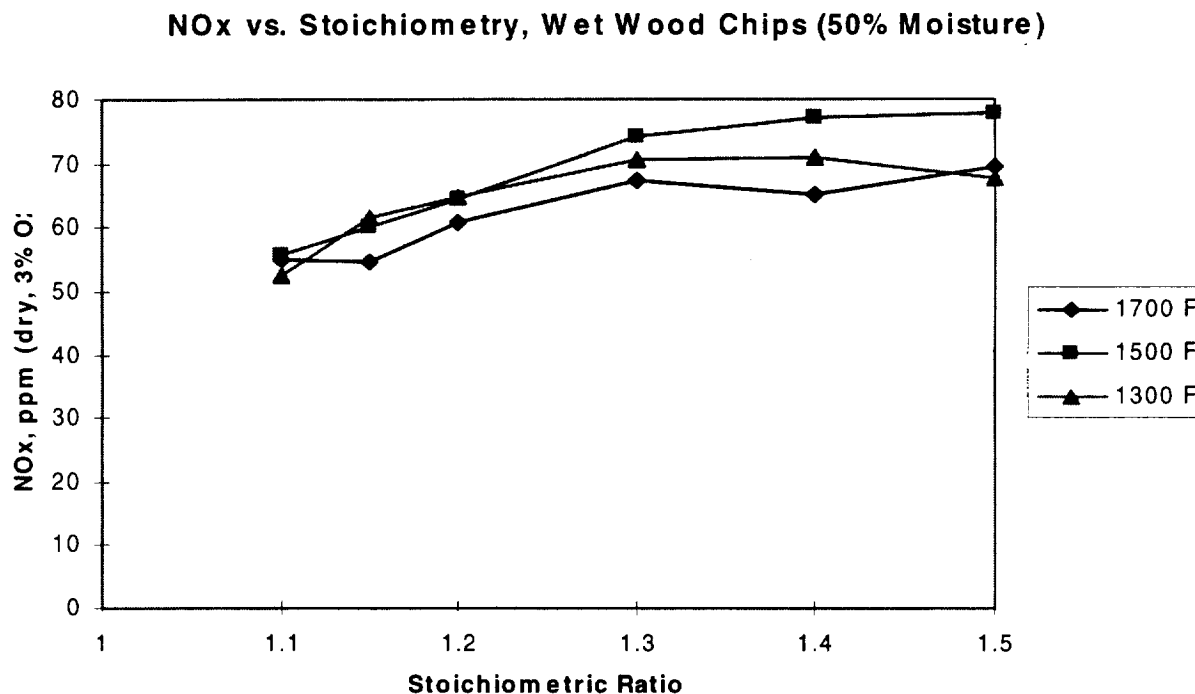


Figure 11. Effect of operating temperature on NO_x emissions when burning wood chips containing 50% moisture.

dependence of NO_x emissions upon temperature is different for the wet (50% moisture) versus dry (5% moisture) wood chips. As was the case with CO emissions, the temperature dependence of NO_x emissions for combustion of 50% moisture wood chips appears to be dependent upon the excess air conditions (i.e., the stoichiometric ratio).

Effects of Moisture

The effects of increasing moisture content on CO emissions is presented in Figure 12 for each of the three temperature conditions investigated. For all of the temperature conditions investigated CO emissions are greater for the 50% moisture cases than for the 5% moisture cases. Increased CO emissions were consistently observed with increased moisture content in the fuel in this system.

The effects of increasing moisture content on NO_x emissions is presented in Figure 13 for each of the three temperature conditions investigated. For all of the temperature conditions

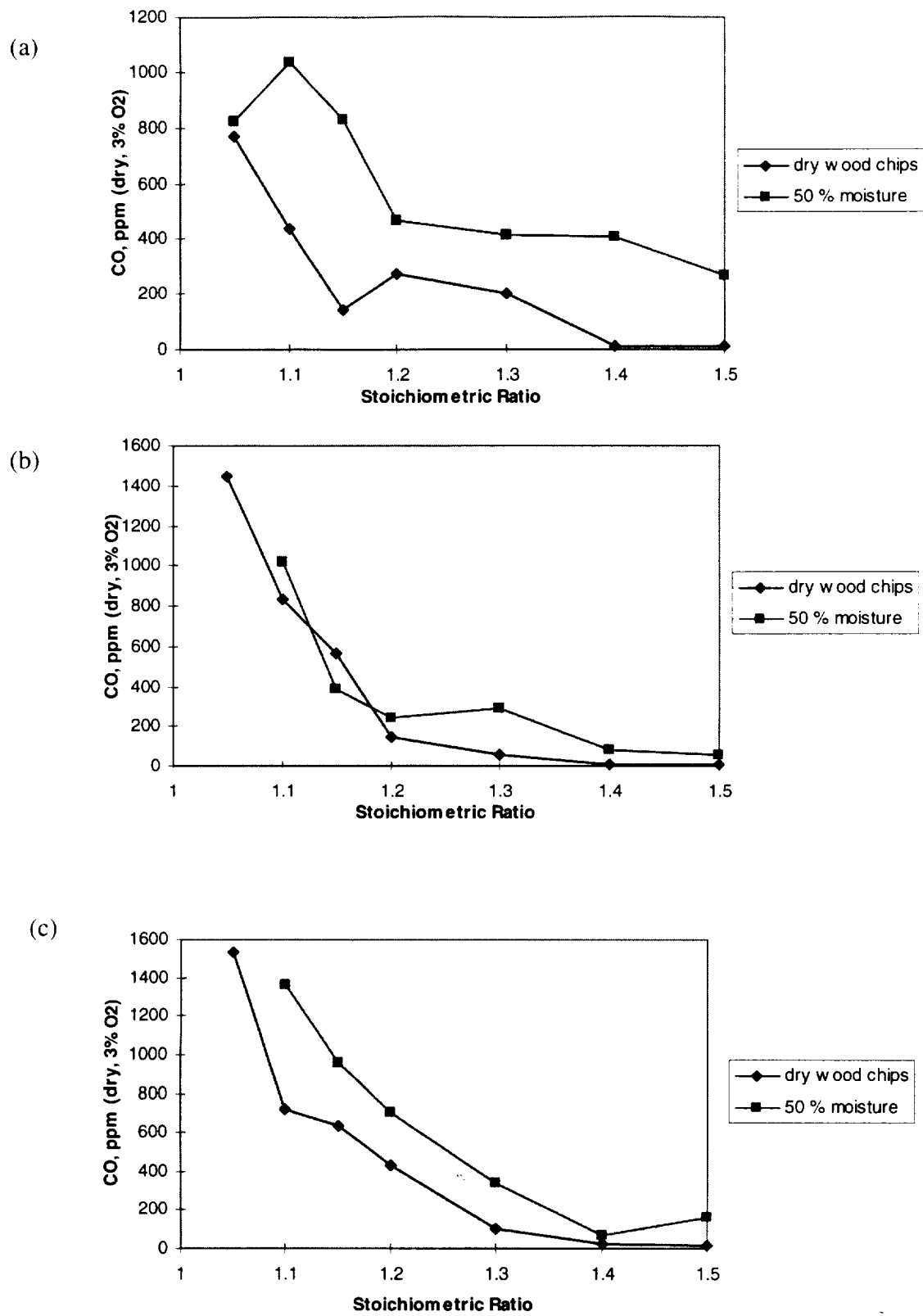


Figure 12. Effect of moisture content on CO emissions for a bed temperature of: (a) 1300°F, (b) 1500°F, and (c) 1700°F.

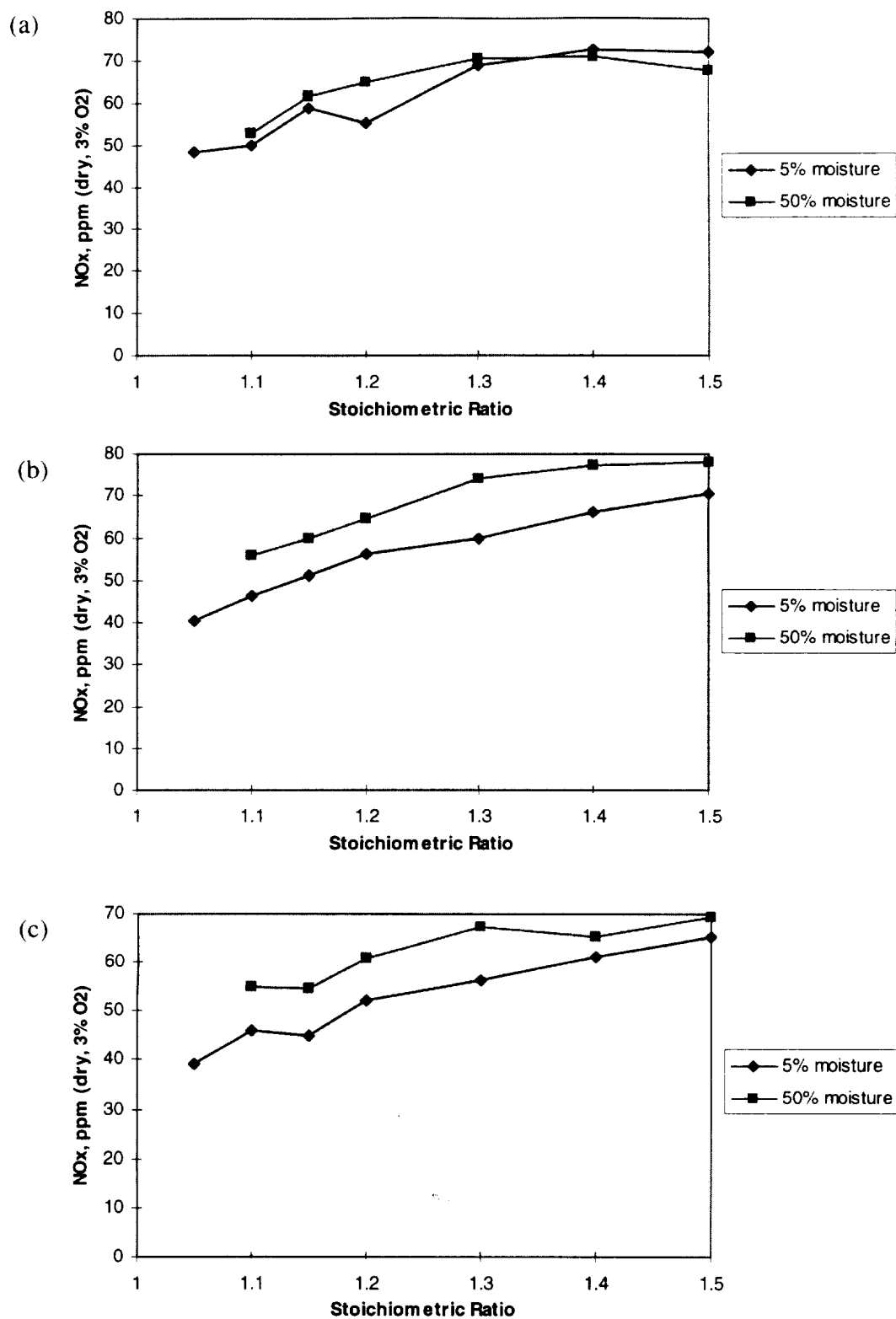


Figure 13. Effect of moisture content on NO_x emissions for a bed temperature of: (a) 1300°F, (b) 1500°F, and (c) 1700°F.

investigated NO_x emissions are greater for the 50% moisture cases than for the 5% moisture cases. This is currently attributed to a proposed lowering of the rate of NO_x reduction in the bed as water levels are increased (Goel et. al., 1996).

Fuel Rich Operation

Fuel-rich operation of the combustor was investigated in order to determine the levels of CO and hydrocarbons that would be produced under fuel-rich conditions. If these hydrocarbons and CO could be accurately controlled to specific levels, they could be used in the catalytic NO_x and SO_x removal process to reduce overall emissions. In this process, CO and hydrocarbons are completely consumed as has been demonstrated in previous studies (Liu and Flytzani-Stephanopoulos, 1995) thus making a low emissions system a nearly zero emissions system when the catalytic clean-up system is optimized.

Rolling average data obtained during fuel-rich combustion of wood chips at a bed temperature of 1500°F are presented in Figure 14. These data indicate large concentrations of

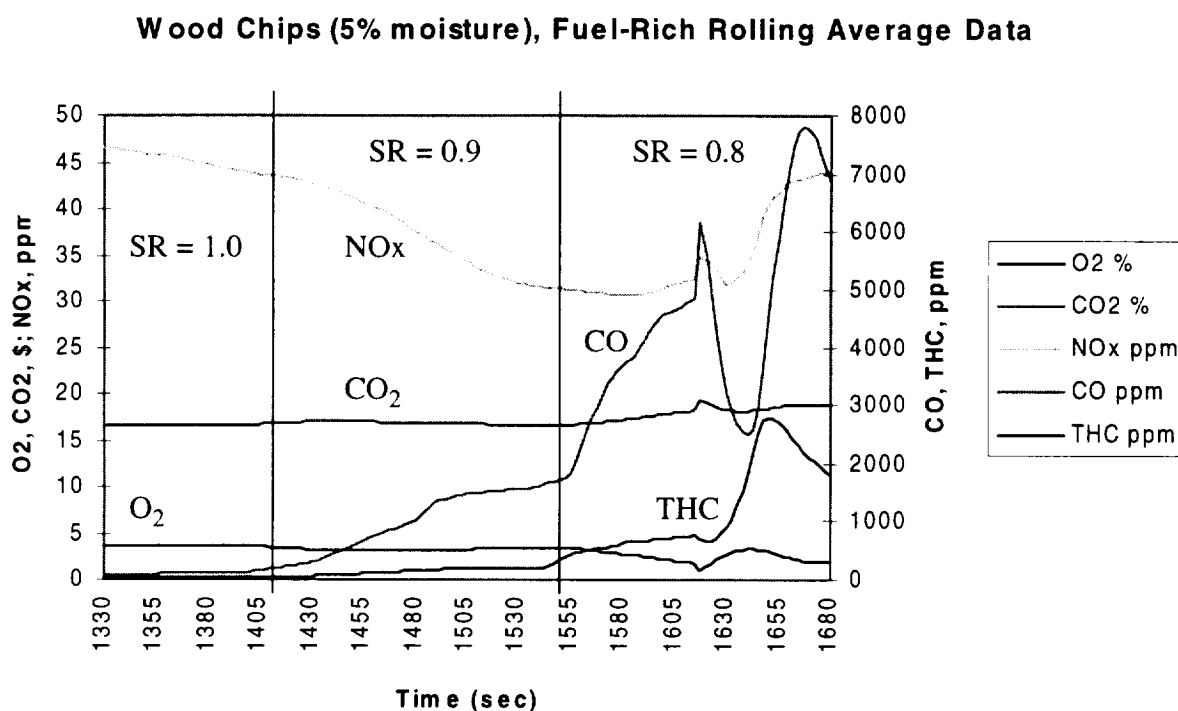


Figure 14. Rolling average data for fuel rich combustion of wood chips (5% moisture) under fuel-rich conditions.

CO and total hydrocarbons (THC) on the fuel rich side of stoichiometric. In Figure 14 the stoichiometric ratio is changed versus time with the first section corresponding to the stoichiometric conditions and subsequent periods corresponding to SR = 0.9 and 0.8. For this

1500°F bed temperature condition, CO values range from 0 to 8000 ppm, and THC ranges from 0 to 3000 ppm.

Average and corrected data obtained during combustion of wood chips at 1500°F bed temperature (including fuel-rich conditions) is presented in Figure 15. These data show the large

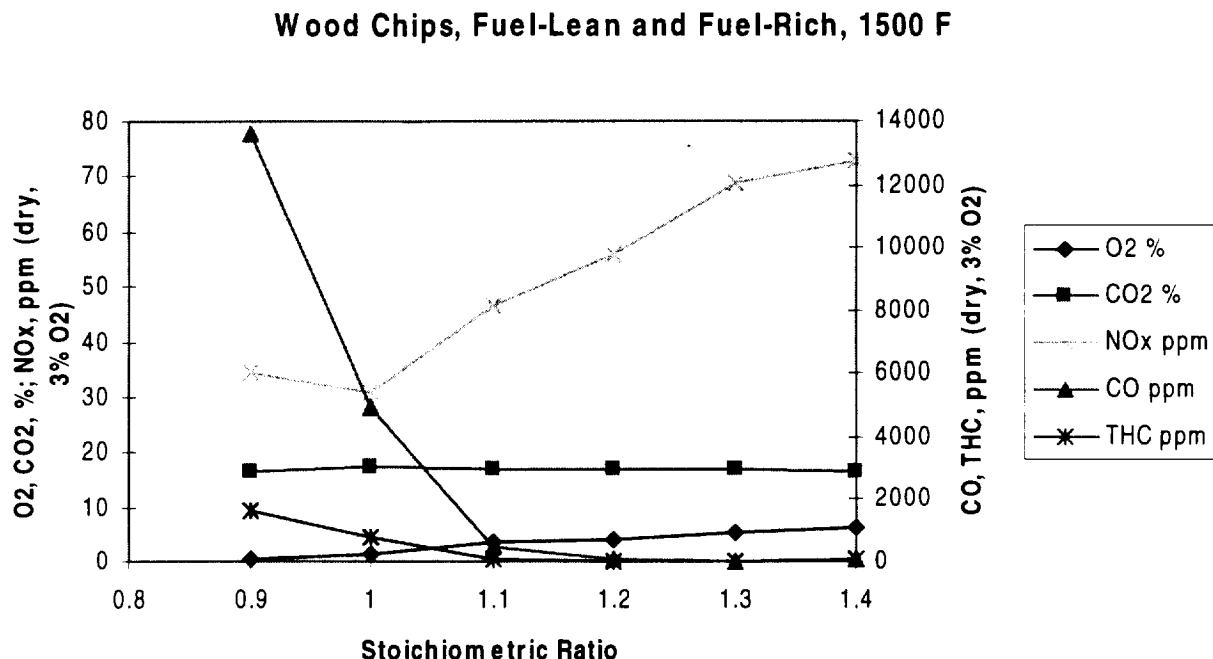


Figure 15. Average corrected data versus stoichiometric ratio for combustion of wood chips at a 1500°F bed temperature, under fuel-lean and fuel-rich conditions.

increases in CO and THC on the fuel-rich side of stoichiometric. Notice that the NO_x concentrations decrease with decreasing excess air for fuel lean conditions but appear to level off or increase as the stoichiometry is decreased into the fuel-rich regime. Figure 16 presents the fuel-rich data only, which highlights the increases in CO, THC and NO_x that are observed as the bed becomes increasingly fuel-rich.

Fuel-rich data were also obtained for a bed temperature of 1300°F and combustion of wood chips with 5% moisture. Figure 17 presents average corrected data for these fuel-lean and fuel-rich conditions. Figure 18 presents the data for fuel-rich conditions only, in which the increasing NO_x, CO and THC trends that were observed for the 1500°F bed temperature conditions are also observed for the 1300°F conditions.

A comparison of the fuel-rich CO, NO_x, and THC data obtained for the 1300 and 1500°F bed conditions is presented in Figure 19. Notice that for fuel-rich conditions CO emissions appear to be greater for the lower bed temperature conditions. NO_x emissions appear to increase with decreasing stoichiometry and are greater for the lower temperature conditions as was observed for

Fuel-Rich, Wood Chips (5% moisture), 1500 F

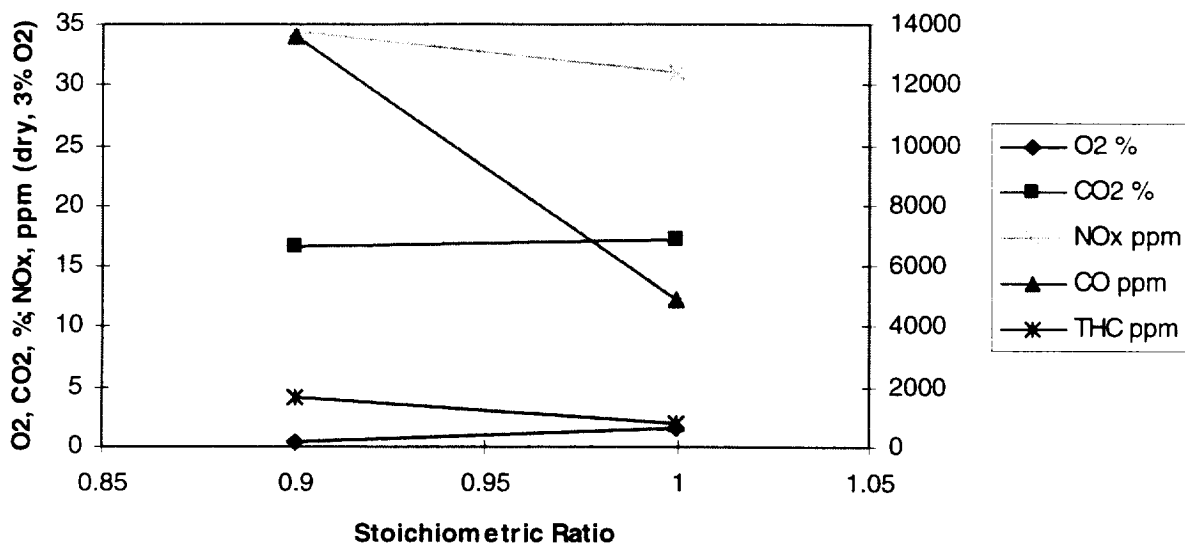


Figure 16. Average corrected data versus stoichiometric ratio for combustion of wood chips at a 1500°F bed temperature, under fuel-rich conditions.

Wood Chips, Fuel-Lean and Fuel-Rich

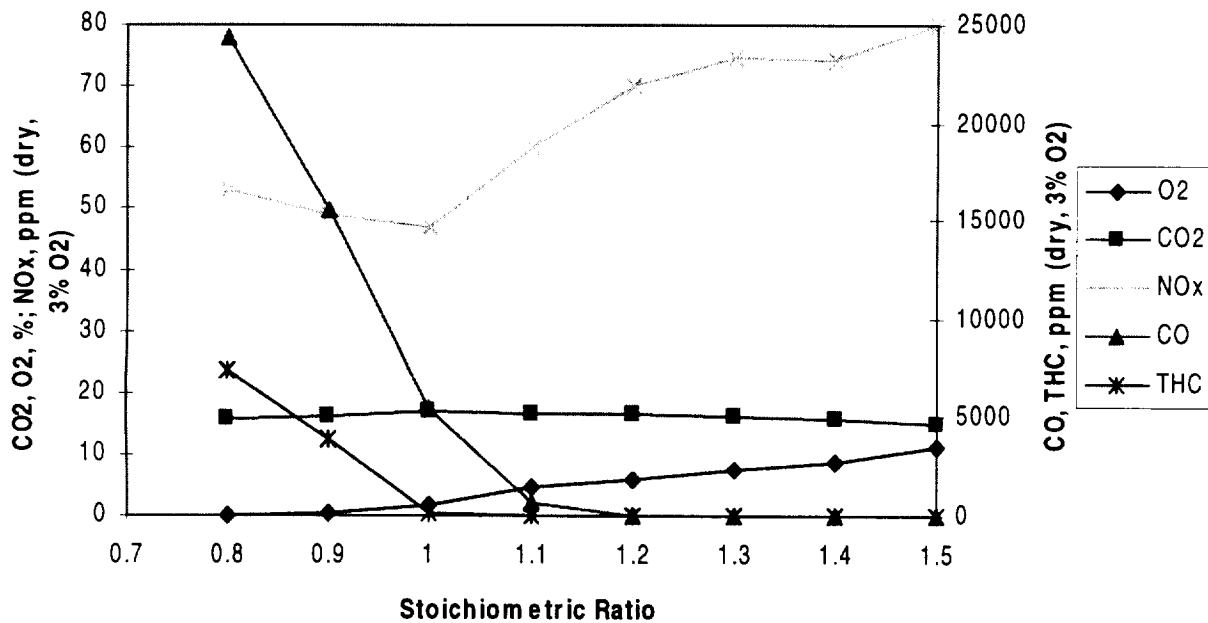


Figure 17. Average corrected data versus stoichiometric ratio for combustion of wood chips at a 1300°F bed temperature, under fuel-lean and fuel-rich conditions.

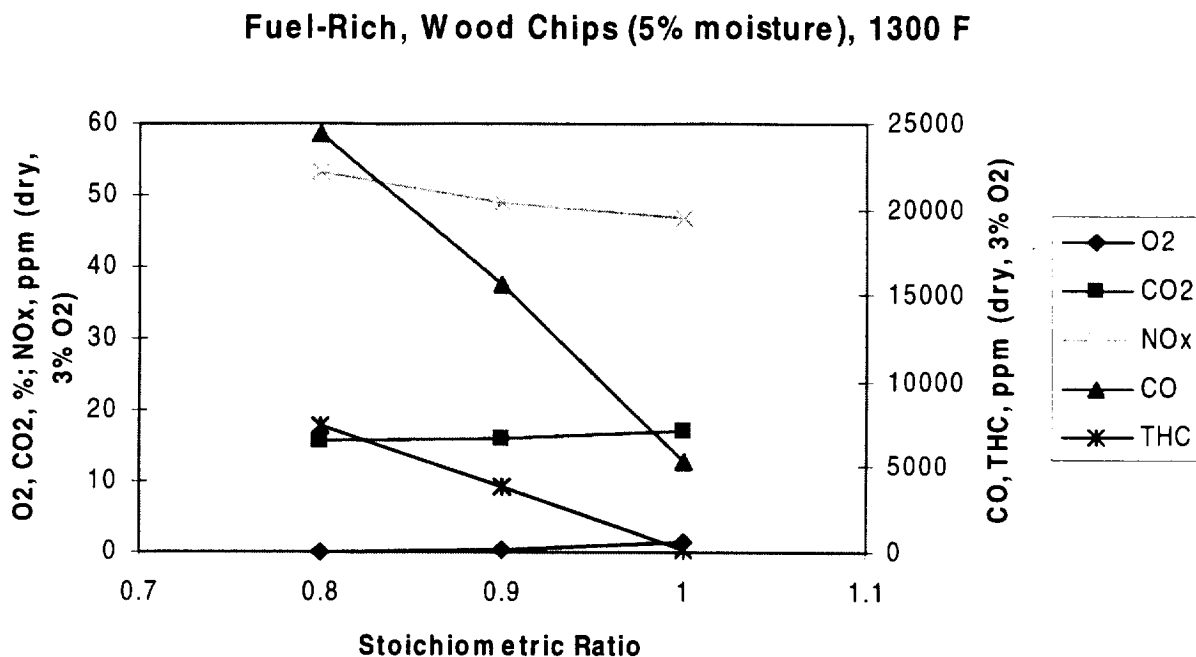


Figure 18. Average corrected data versus stoichiometric ratio for combustion of wood chips at a 1300°F bed temperature, under fuel-rich conditions.

fuel-lean conditions. The THC emissions are substantial for fuel-rich operation as compared to fuel-lean operation when THC emissions were consistently below 10 ppm. THC concentrations appear to be greater for the lower temperature conditions which is consistent with the CO emissions data.

Effect of Fuel Type

A significant problem involving the combustion of the inedible biomass portion of the waste stream is the possible slagging that could occur in the reactor due to the high potassium content of the inedible biomass. In order to minimize melting of the high potassium ash in the reactor, temperatures should be maintained below the fusion point of the ash which contains high levels of potassium (fusion points of some representative materials are: potassium oxide = 806°F, potassium chloride = 1418°F). Muffle furnace tests containing crucibles of the actual hydroponic biomass material showed significant ash fusion at 1472°F, but below 1292°F ash fusion was not observed. Therefore, it was decided to operate the fluidized bed at a temperature of 1300°F or lower during combustion of high potassium containing fuel streams.

Hay was combusted at 1150°F and 1300°F bed temperatures in the fluidized bed reactor. Average corrected results from the 1150°F tests are presented in Figure 20. The upper panel which presents O₂, CO₂ and NO_x results indicates a relatively good mass balance and close to complete

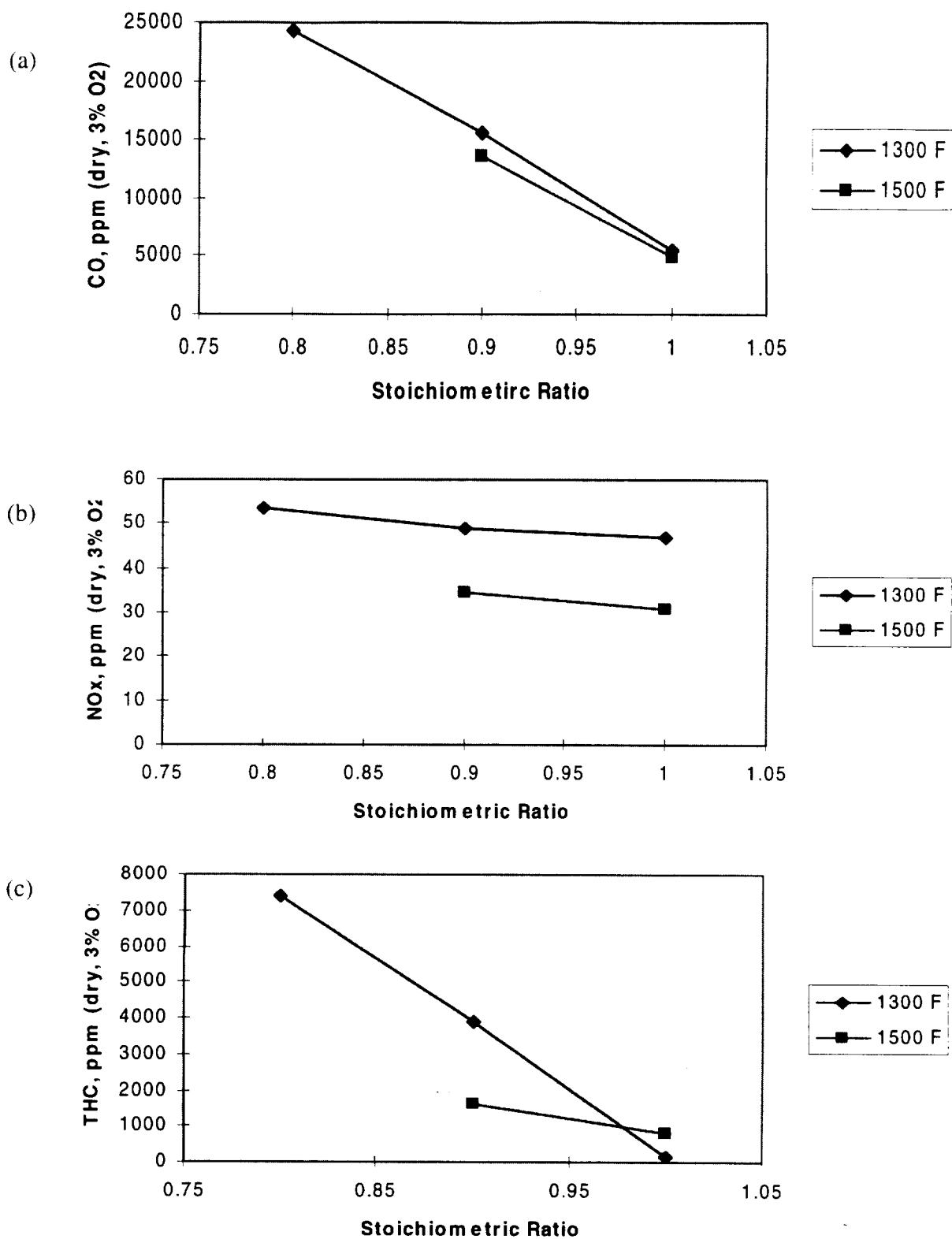


Figure 19. Effect of temperature on CO, NO_x, and THC emissions for fuel-rich combustion of wood chips with 5% moisture: (a) CO, (b) NO_x, (c) THC.

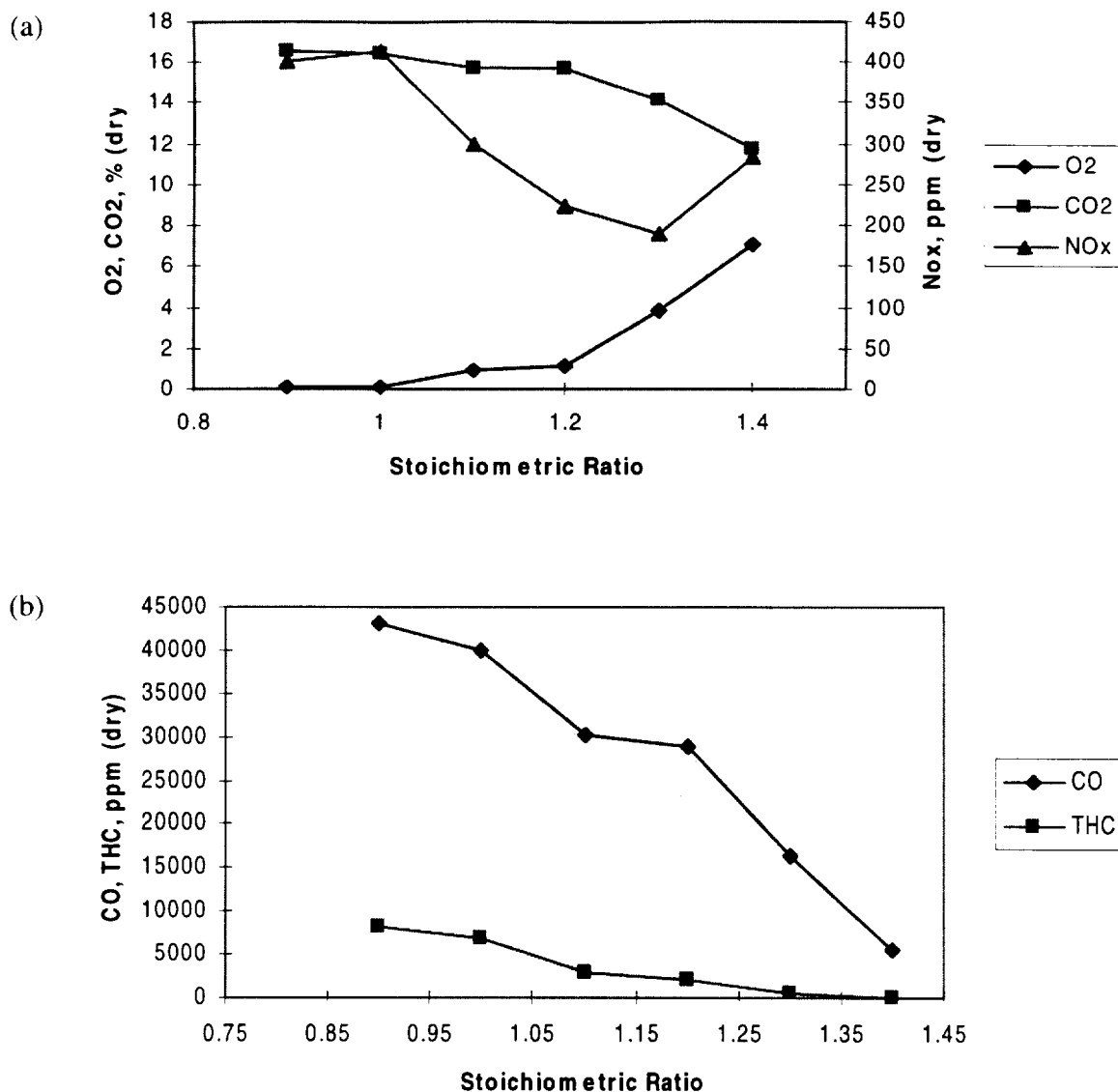


Figure 20. Average data for combustion of hay at a bed temperature of 1150°F: (a) O₂, CO₂, and NO_x, (b) CO and total hydrocarbons.

combustion. Calculated complete combustion values for CO₂ and O₂ for the SR = 1.4 case, for instance, are 12.3 and 6.9% respectively compared to the measured values of 11.9 and 7.1%. However, the CO and total hydrocarbon concentrations observed for these low bed temperature conditions with combustion of hay are substantially higher than those measured for higher bed temperatures (1300-1700°F) with the combustion of wood chips. The lower panel of Figure 20 shows CO concentrations in the range of 5000 to 45000 ppm (0.5 to 4.5%) and THC concentrations ranging from 0 to 8000 ppm. Notice that even for fuel-lean conditions, CO and THC emissions are high.

As shown in Figure 20 (a), NO_x emissions for the combustion of hay are in the range of 200 to 400 ppm. This range is substantially greater than that observed for combustion of wood chips and is due to the higher fuel-nitrogen content of the hay compared to the wood (1.6% versus 0.1%). The higher NO_x emissions for the higher fuel-nitrogen containing fuel also indicates the importance of the fuel nitrogen NO_x formation mechanism for these conditions. The dependence of the NO_x emissions on stoichiometric ratio also appears to be different than that of the wood with NO_x emissions that appear to peak at the stoichiometric condition.

Data was also obtained for combustion of hay at a bed temperature of 1300°F. Figure 21 presents the averaged data for these conditions versus stoichiometric ratio. These data show the same trends as in the hay combustion case at 1150°F bed temperature. The NO_x appears to peak at the stoichiometric condition and the CO₂ and O₂ suggest reasonably complete combustion. The CO and THC data show high levels of these products even for high excess air conditions. The levels of CO and THC are substantially greater than those obtained during combustion of wood chips. Note that the leveling off of the CO and THC emissions as the bed is made more fuel-rich (i.e., as SR is decreased) is due to the maximum measurable levels of CO and THC for the current instruments contained in the laboratory. The maximum measurable CO is 50000 ppm (5%) while the maximum THC reading is 10000 ppm (1%). As was observed for wood chip combustion, the CO and THC emissions are greater for the higher bed temperature conditions.

At bed temperatures above 1300°F slagging in the bed was consistently observed with combustion of the high potassium containing hay with a sand bed material. Bed temperatures in the range of 1350°F to 1400°F led to coagulation of bed material and subsequent failure of the bed to fluidize. Figure 22 presents data which indicate this failure when combusting hay at 1350°F in a sand bed. The initial condition was for a stoichiometric ratio (SR) of 1.4, with subsequent reductions in the SR to 1.3, 1.2 and 1.1 at times of 250 seconds, 680 seconds, and 1000 seconds. Bed failure appears to occur at a time of about 950 seconds as the stoichiometric condition was approached from fuel-lean conditions.

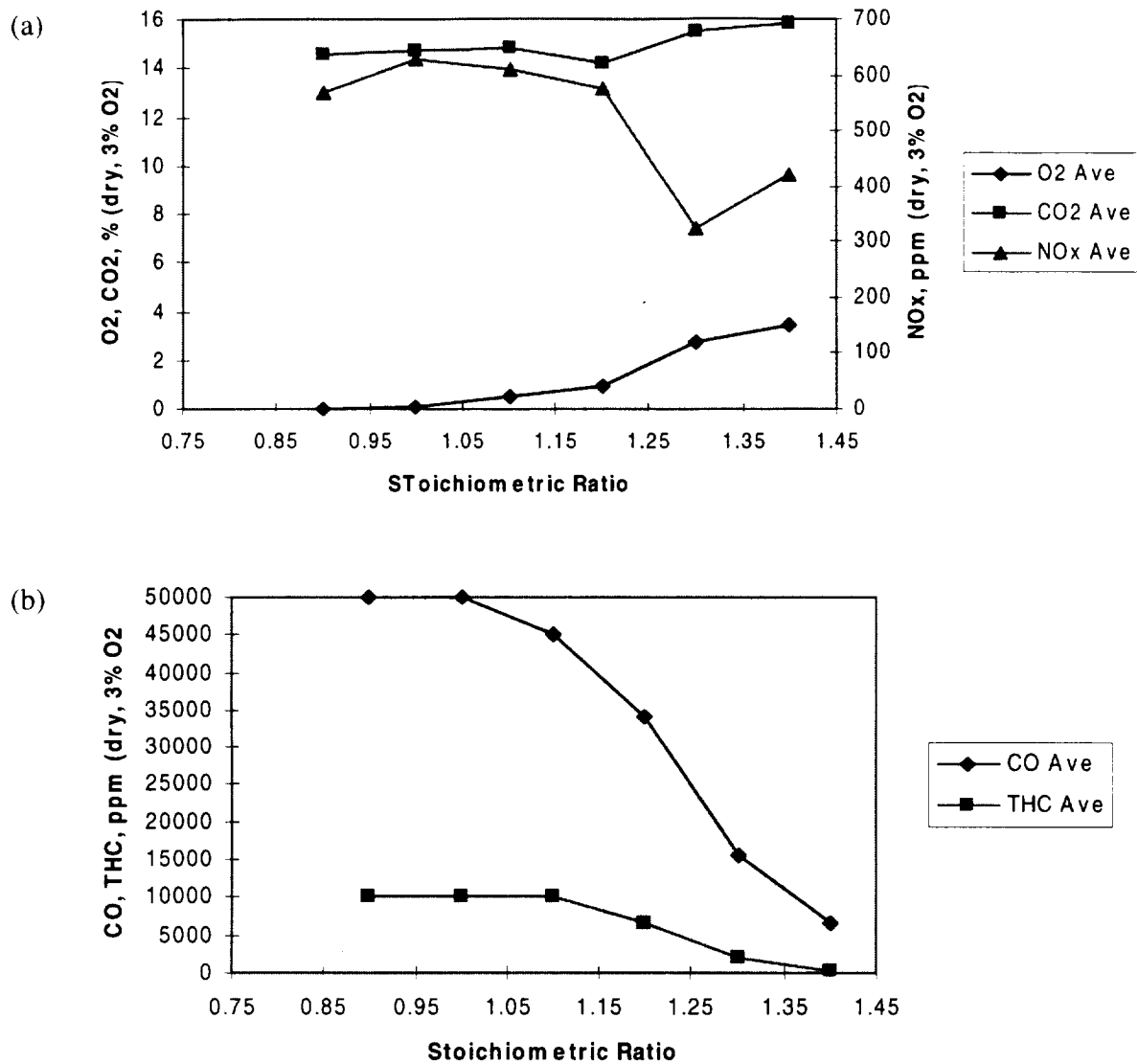


Figure 21. Average data for combustion of hay at a bed temperature of 1300°F: (a) O₂, CO₂, and NO_x, (b) CO and total hydrocarbons.

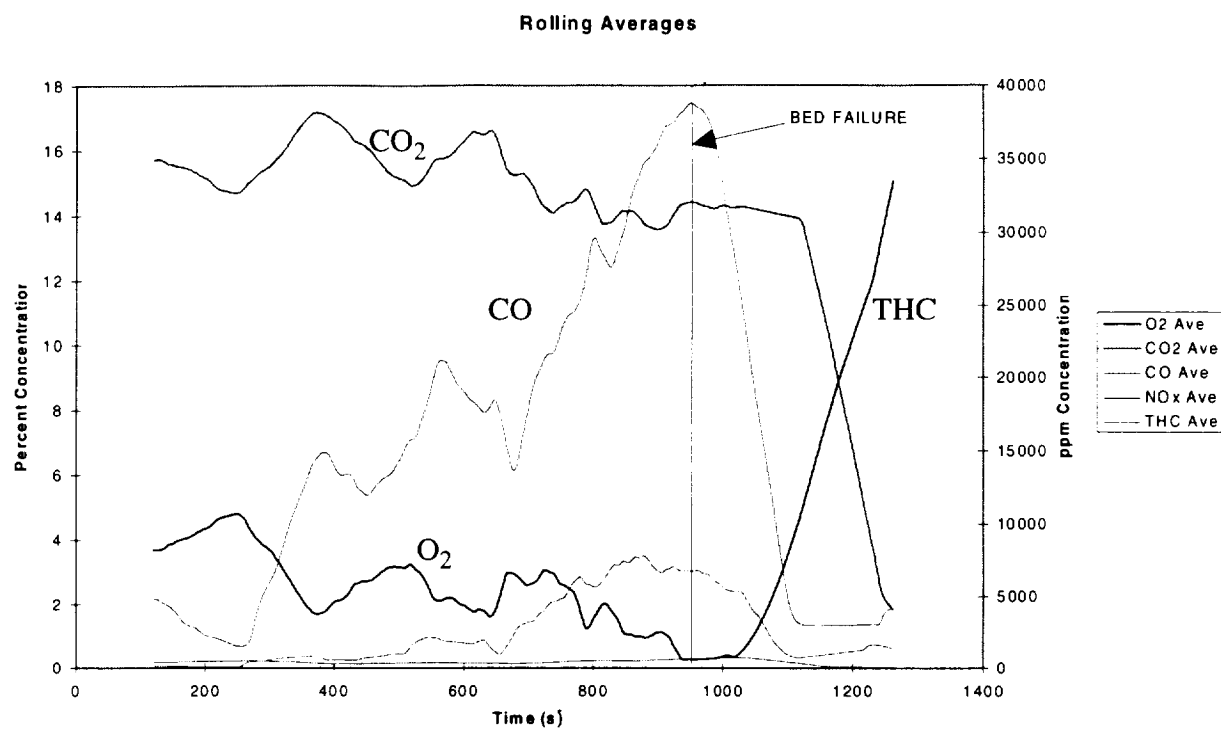


Figure 22. Rolling Average data obtained for hay combustion at a bed temperature of 1350oF indicating failure of the bed as stoichiometric conditions were approached.

Future Combustor Work

Over the next year, several tasks will be accomplished to complete the work:

- feeding system will be finalized and a method to feed human waste developed;
- different bed materials will be investigated to determine if changing the bed from sand eliminates the slagging of the material;
- optimization of the combustion system will take place, integrating the emissions with maximum operating temperatures; and
- waste variables will be investigated including moisture content, nitrogen content, and other trace components of the materials.

Gas Cleanup System

A preliminary test has been conducted on the copper oxide system and the results are presented in Figure 23. As seen in this figure, the sulfur was immediately reduced below the detection limits of the FTIR. Sulfur dioxide breakthrough occurred after approximately 70% of the copper oxide was utilized (initial concentration of SO_2 was 330 ppm). As shown in the figure, the NO reduction occurred only after the copper oxide was sulfated (to become the catalyst). The initial concentrations of NO and ammonia were 160 ppm and 170 ppm respectively. Once reduction took place, the NO dropped to below 3 ppm (presently the detection limits of the FTIR). No ammonia “slip” was seen. Future experiments will include a layer of sulfated copper oxide to reduce the NO immediately. These experiments will continue and several variables will be investigated over the next year:

- optimization of the temperature, amount of ammonia required, optimal amount of copper oxide on sorbent;
- influence of HCl on the reduction of sulfur dioxide and NO; and
- integration of a full-scale system with the incinerator and final cleanup design requirements identified.

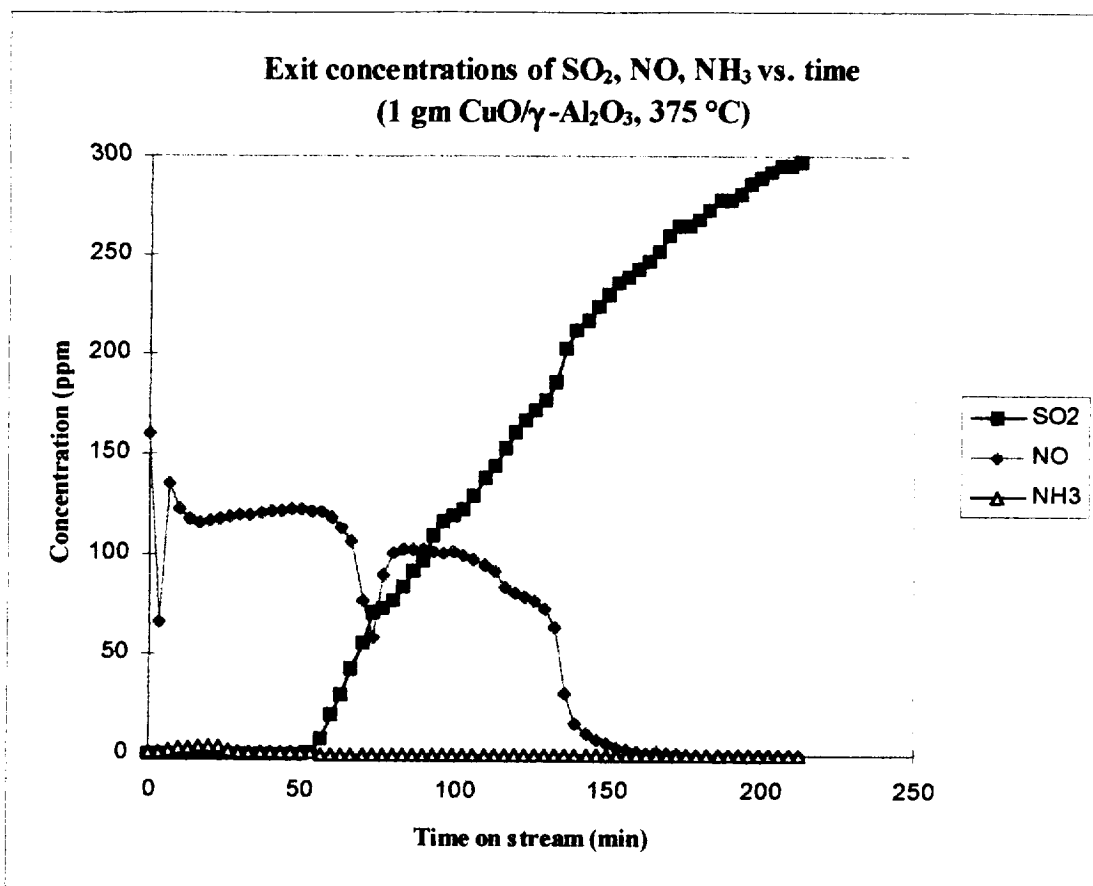


Figure 23. Results of preliminary copper oxide catalyst test.
Exhaust concentrations of SO₂, NO, and NH₃ as a function of time.